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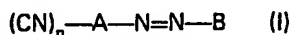
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 (22) Date of filing 29 May 1979
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(54) Process for the Manufacture of
 Cyanoazo Dyestuffs

(57) A process for the manufacture of a
 water-insoluble cyanoazo dyestuff of
 the formula (I)



comprises reacting a compound of the
 formula (II)

coupling component, A and B are free
 from water-solubilising groups and
 optionally contain other substituents
 usual in azo dyestuffs and n is 1 or 2
 with an alkaline cyanide in a solvent of
 the formula (III)



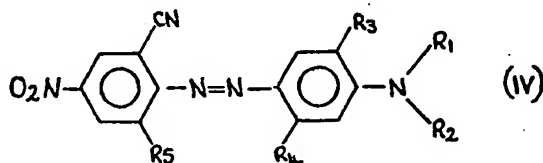
where R and R' represent alkylene
 radicals having from 1 to 8 carbon
 id

(52) C
 C
 3
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 7
 C
 (56) C
 G
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 (58) F
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 (72) Ir
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 (74) A
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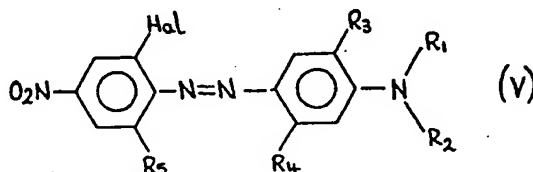
ERRATA

SPECIFICATION No. 2 022 089 A

Page 5, line 63, *delete existing formula insert*



Page 5, line 66, *delete existing formula insert*



THE PATENT OFFICE
 25th February, 1980

The chemical formulae appearing
 in the printed specification were
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 the date of filing.

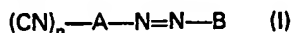
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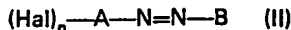
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(54) Process for the Manufacture of
 Cyanoazo Dyestuffs

(57) A process for the manufacture of a
 water-insoluble cyanoazo dyestuff of
 the formula (I)



comprises reacting a compound of the
 formula (II)



in which A represents a benzenic
 radical containing one or more nitrile
 or halogen substituents ortho to the
 azo group, Hal represents a halogen
 atom, B represents the radical of a

coupling component, A and B are free
 from water-solubilising groups and
 optionally contain other substituents
 usual in azo dyestuffs and n is 1 or 2
 with an alkaline cyanide in a solvent of
 the formula (III)



where R and R' represent alkylene
 radicals having from 1 to 8 carbon
 atoms, with a straight or branched
 chain able to contain a —O— or
 —S— bridge and X represents a
 hydrogen atom or a hydroxyl group in
 the presence of a novel catalyst
 formed by a combination between a
 thioether of formula (III) and a cuprous
 salt.

The chemical formulae appearing
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GB 2 022 089 A

SPECIFICATION

Process for the Manufacture of Cyano Azo Dyestuffs

5 The invention relates to a process for the manufacture of cyano azo dyestuffs.

The preparation of organic cyano compounds by treatment of the corresponding halogen compounds with a metal cyanide, preferably cuprous cyanide used as such or in the form of a mineral or organic complex, is well known from the literature. The application of these cyanising methods to water-insoluble halogenated azo dyestuffs of which the halogen atoms are in the ortho position with respect to the azo group, has also been described in numerous patents, for example in French Patents Nos. 1,511,932, 2,196,325, 2,258,430 and 2,343,783.

However, these processes at the industrial level have a certain number of disadvantages. In particular, after each reaction, the recovery of the solvents used which are mixed with the water or another solvent is difficult and costly. Further, the frequently recommended use of the cuprous cyanide with strongly polar solvents leads to the formation of undesirable secondary products which reduce the yield and the quality of the dyestuffs. Another important disadvantage is that in these processes the copper necessary to the reaction as a catalyst is again found in the dyestuffs as a water-insoluble cuprous halide and it has to be eliminated either directly from the reaction medium or from the isolated dyestuff pastes. This treatment for removal of the copper by a further complete treatment of the dyestuff in a medium in which the cuprous salts are oxidised or form a complex or by washing the crude cake of dyestuff with an organic solvent constitutes industrially a long, delicate and costly purification process. In any case, the copper is lost, which indicates that, for each industrial operation a fresh consumption of copper is required.

U.S. Patent No. 3,772,268 describes a cyanisation process leading to dyestuffs containing scarcely any copper owing to the use as solvent of a mixture containing a di(hydroxyalkyl)-sulphide in the presence of a cyanide and a catalyst formed by complexing a copper salt and di(hydroxyalkyl) sulphide. The recovery of the dye is made by dilution of the reaction medium with water and filtration, which permits a direct and easy elimination of the cuprous complex and of the solvent since these are soluble in the water. However, this process has disadvantages at the industrial level. In fact, the recovery of the solvent solubilised in the water is difficult and costly; the absence of recovery causes industrial pollution and makes the expenses of manufacture heavy. Further, the cuprous complex serving as catalyst cannot be recovered and the copper is found in the effluents from the treatment, which gives a pollution problem.

French Patent Application No. 2,347,415 describes an improved process owing to the use as solvent of bis(cyanoalkyl)-sulphide in the

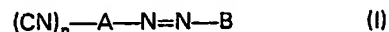
65 presence of water, alkaline cyanide and a cuprous salt forming a complex with the solvent. These solvents permit a direct isolation of the cyano dyestuffs obtained without it being necessary to cause crystallisation by dilution with water or

70 another solvent. In addition, the cuprous complexes, soluble in the sulphide are stable and highly reactive for catalysing the cyanisation reaction and are found without change or loss in the reaction solvent after isolation of the manufactured dyestuff. From these properties it follows that the solvent and the cuprous complex are recovered and can be used again.

Nevertheless, the use of these bis(cyanoalkyl)-sulphides shows, at the industrial level, some drawbacks which are related to the presence of the nitrile groups in these molecules and to the physico-chemical properties which follow therefrom. In fact, these sulphides are not in general liquid at temperatures above the ambient temperature, so that their use as solvent necessitates maintaining the temperature above the crystallisation temperature during the whole time of manipulation and storage. On the other hand, these solvents are not strictly inert towards the reaction medium; a slight hydrolysis of the nitrile groups, activated in the presence of the copper derivatives, is produced and the recovery of the solvents then becomes more difficult.

We have now found a new industrial process which is more economical and nonpolluting and permits easy recovery of the solvent and of the copper catalyst used and the obtaining of cyano dyestuffs of high purity, i.e. substantially free of secondary products and metal.

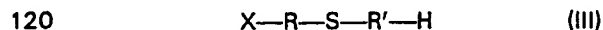
100 According to the present invention therefore a process is provided for the manufacture of a water-insoluble cyano azo dyestuff of the formula (I)



105 which comprises reacting a halogenated azo compound of the formula (II)



in which A represents a benzenic radical containing one or more nitrile or halogen substituents in the ortho position with respect to the azo group, Hal represents a halogen atom, especially bromine, chlorine or iodine, B represents the radical of a coupling component, preferably a substituted para-amino arylene radical, A and B are free from water-solubilising groups and optionally carry other substituents usual in azo dyestuffs and n is 1 or 2, with an alkaline cyanide, preferably sodium cyanide, in a solvent comprising a thio-ether of formula (III):



in which R and R', which may be the same or different, each represent an alkylene radical, having from one to eight carbons atoms, with a

straight or branched chain able to contain an —O— or —S— bridge, and X represents a hydrogen atom or a hydroxyl group, and in the presence of a catalyst formed by a combination between a thio-ether of formula (III) and a cuprous salt.

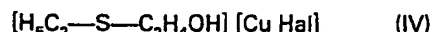
Examples of the radicals of coupling components B are aniline and its *n*-alkyl derivatives for example *n*-methyl aniline, *n*-ethyl-aniline, *n,n*-dimethyl-aniline, *n,n*-diethylaniline, *n*-(beta-hydroxy-ethyl)-aniline, *n*-methyl-*n*-(beta-hydroxyethyl)-aniline, *n*-ethyl-*n*-(beta-hydroxyethyl)-aniline, *n*-butyl-*n*-(beta-hydroxy-ethyl)-aniline, *n,n*-bis-(beta-hydroxyethyl)-aniline, *n*-(beta-cyanethyl)-aniline, *n*-methyl-*n*-(beta-cyanethyl)-aniline, *n,n*-bis-(beta-cyanethyl)-aniline, *n*-(beta-hydroxyethyl-*n*-(beta-cyanethyl)-aniline, *n*-(beta-carbomethoxyethyl)-aniline, *n*-ethyl-*n*-(beta-carbomethoxyethyl)-aniline, *n*-(beta-cyanethyl)-*n*-(beta-carbomethoxyethyl)-aniline, *n,n*-bis-(beta-carbomethoxy-ethyl)-aniline, *n*-ethyl-*n*-(beta-acetoxyethyl)-aniline, *n*-(beta-cyanethyl) *n*-(beta-acetoxyethyl)-aniline, *n,n*-bis-(beta-acetoxyethyl)-aniline *n*-ethyl-*n*-(beta-methoxyethyl)-aniline, *n,n*-bis(2,3-dihydroxy-propyl)-aniline, *n*-ethyl-*n*-(2-hydroxy-3-chloropropyl)-aniline, *n*-benzyl-*n*-(beta-cyanethyl)-aniline, 3-methyl-aniline, 2,5-dimethyl-aniline, 2-methoxy-aniline, 3-ethoxy-aniline, 5-methyl-2-methoxy-aniline, 5-methyl-2-ethoxy-aniline, 2,5-dimethoxy-aniline, 3-acetyl-amino-aniline, 2-methoxy-5-acetyl-amino-aniline, 2-ethoxy-5-acetyl-amino-aniline and the corresponding *n*-substituted derivatives of these amines; diphenylamine, 1-amino-naphthalene and its *n*-substituted derivatives for example 1-(*n,n*-dimethylamino)-naphthalene or 1-(*n*-beta-hydroxyethylamino)-naphthalene, 1,2,3,4-tetrahydro-quinoline and its *n*-substituted derivatives for example *n*-(beta-hydroxyethyl)-1,2,3,4-tetrahydro-quinoline and *n*-(beta-cyanethyl)-1,2,3,4-tetrahydro-quinoline; hydroxy-benzene, 1-hydroxy-2-methyl-benzene, 1-hydroxy-methyl-benzene, 1-hydroxy-3-acetyl-amino-benzene, 1-hydroxy-3-methoxy-benzene, 1-hydroxy-2,5-dimethyl-benzene, 1-hydroxy-naphthalene, 8-hydroxy-quinoline, 2-methyl-indole and 2-phenyl-indole.

Examples of thioethers of formula (III) are diethyl sulphide, dipropyl sulphide, ethyl propyl sulphide, di-*n*-amyl sulphide, ethyl isoamyl sulphide, propyl isoamyl sulphide, diisoamyl sulphide, dihexyl sulphide, ethyl β -hydroxyethyl sulphide, butyl β -hydroxyethyl sulphide, methyl β -hydroxyethyl sulphide, di- β -hydroxy- β -methoxy diethyl sulphide, di- β -hydroxy- β -ethoxy diethyl sulphide, di- β -ethoxy-ethyl sulphide, butyl β -hydroxyethyl sulphide, butyl β -ethoxyethyl sulphide, *sec*.-butyl β -hydroxyethyl sulphide, *ter*butyl β -hydroxy-ethyl sulphide, di-thioethyleneglycol dimethylether; ethyl β -hydroxyethyl sulphide, which is a current product manufactured in the chemical industry, is particularly preferred. These compounds, although already known in the literature, have

never to the knowledge of the applicant been described for the preparation of cyano azo compounds.

The thioethers of formula (III) constitute reaction media of great value, since they are, at the reaction temperature, excellent solvents for halogenated compounds of formula (II) and corresponding cyano compounds of formula (I), so that the cyanisation reaction may be taken to its end without risk of blocking owing to a partial insolubilisation of the substances used. They have the property of causing a rapid start of reaction of the reagents, without so much as producing secondary reactions, so that the products obtained are very pure. They also permit the dyestuffs of formula (I) to be isolated at the ambient temperature directly by filtration, without it being necessary to add water or another solvent. Further, these solvents are perfectly stable in the medium in spite of the presence of copper derivatives; thus, their direct recycling is effected easily and practically without limits.

On the other hand, we have established that the cuprous complexes act as very active catalysts of the cyanisation reaction. By way of example, the molecular combination of formula (IV) may be mentioned:



We have also found that the cuprous complexes are themselves soluble in the thioethers of formula (III) and that the solutions obtained are perfectly stable, even after several months of use, so that it is possible, when a reaction is finished and after cooling then filtration of the dyestuff, to recover them practically completely, at the same time as the solvent which contains them. The quality of solvent obtained is such that it can be directly recycled a large number of times. In other words, from a practical point of view the cyanisation reaction only consumes the alkaline cyanide and the consumption of cuprous derivative and solvent becomes very small, even negligible.

In the practice of one embodiment of the new process of this invention first of all essentially in the first operation the organic copper complex is prepared. This is effected by the addition of a cuprous salt in an excess of thioether of the formula (III); it may be advantageous, but not essential, to heat slightly to 40—60°C. in order to reduce the time of formation of the complex. One may also, optionally, introduce the previously isolated catalyst directly into the reaction solvent. Then the halogenated azo compound is added and then the alkaline cyanide and the temperature is taken to the reaction temperature. The completion of the reaction is controlled by thin layer chromatography and then the reaction mass is cooled. The cyano dyestuff, which has precipitated, and the alkaline halide formed during the substitution are separated by filtration; the filtrate contains nearly the whole of the solvent and the complex used in the reaction. The

dyestuff is then washed with water, sodium chloride being added to the wash water if desired, and the last parts of solvent can be recovered by decantation since it is insoluble or very slightly soluble in this medium. The solvent fractions thus recovered contain, besides a little dissolved cyano-dyestuff, all the catalyst put in at the beginning; its purity is such that it may be directly recycled for further operations, without any particular treatment or fresh addition of catalyst.

The dyestuff produced is generally of great purity; its content of residual copper salts (expressed as elementary copper) does not exceed 0.1%.

The reaction temperature may also be varied over a wide range; this temperature must be adapted to the case, chiefly according to the structure and also the nature of the halogen of the compound of formula (II). It is general to work at temperatures between 60°C and 150°C and preferably between 80°C and 100°C.

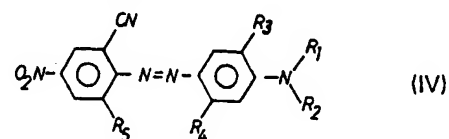
By "alkaline" cyanides we mean the cyanides of lithium, ammonium, and above all those of potassium and sodium. To obtain a complete reaction, it is generally sufficient to use the stoichiometric amount of cyanide; this proportion, however, may be slightly increased in some cases, e.g. when the speed of reaction is low, without affecting the process, up to twice the stoichiometric amount. In the molecular combination of copper and thioether, the cuprous salt to be used may, without affecting the result of the reaction, be for example a halide or a derivative of a carboxylic acid such as, for example, the acetate. For practical reasons, however, it is preferred to use cuprous bromide or cuprous chloride. The molecular combinations may in general be isolated in the form of crystalline products which are stable and with a definite melting point, for example from their concentrated solutions of thioethers. As has been previously said, it is not, however, essential to isolate them. The quantity of catalyst necessary so that the cyanisation reaction takes place may be very small; in practice, in order to obtain a suitable speed of cyanisation and good yields of cyano-dyestuff, it has been found that the proportion of catalyst usually has to be from 0.1 to 0.8 and preferably from 0.25 to 0.5 atoms of copper per mole of halogenated dyestuff used.

The halogenated azo compounds of formula (II) may be prepared in a known manner, for example by diazotisation of an orthohaloaniline, then coupling the diazo compound obtained with a coupling component. The radicals A and B of the formula (I) may contain substituents usual for the class of disperse azo dyestuffs, for example halo, nitro, cyano, trifluoroalkyl, or sulphonyl for A and acylamino, acyl, secondary or tertiary amino, alkyl, alkoxy, aryl, aralkyl or ester of carboxylic acid for B.

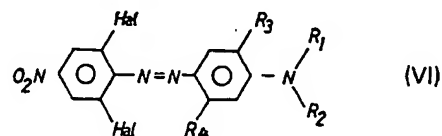
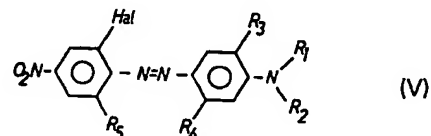
The dyestuffs of formula (I) are chiefly used in dispersed form for the colouration of cellulose esters and polyesters.

According to a preferred form of the new

process, the cyano azo dyestuff of formula (I) corresponds to the formula



and the halogenated azo compound of formula (II) corresponds to one of the formulae:



in which:

R₁ represents hydrogen, a phenylalkyl group, an unsubstituted alkyl group simple, or an alkyl group substituted by OH, Cl, F, CN, COOR₆, OCOR₆, OCO₂R₆, OR₆ or OCOCH=CH-phenyl.

R₂ either has the same significance as R₁, or represents a phenyl or cyclohexyl group;

R₃ represents a hydrogen atom or an alkyl, alkoxy, alkoxycarbonyl, aryloxy or aralkoxy group, for example, R₃ may be hydrogen, CH₃, OCH₃, OC₂H₅ or COO-alkyl;

R₄ represents H, CH₃, OCH₃, OC₂H₅, Cl

NHSO₂R₆, NHCOOR₆ or NHCOR₆;

R₅ represents H, CF₃, COR₆, CN, NO₂ or SO₂R₆; and

R₆ is an alkyl, cyclohexyl, phenyl, tolyl or methoxyphenyl radical.

In the definition of R₁ in the above formulae the alkyl group preferably has 1 to 4 carbon atoms and the phenylalkyl group is preferably one in which the alkyl group has 1 or 2 carbon atoms.

In the definition of R₃ the alkyl and alkoxy groups preferably have 1 to 4 carbon atoms and the preferred aryloxy and aralkoxy groups are the phenyloxy, phenylmethoxy phenylethoxy groups. In the definition of R₅ the alkyl group preferably has 1 or 2 carbon atoms.

The invention is illustrated by the following Examples, in which the parts are parts by weight unless the contrary is specified.

Example 1

357 parts of ethyl β-hydroxyethyl sulphide, 2.23 parts of cuprous chloride, 2.15 parts of 3-acetamide-4-(2'-bromo 4',6'-dinitrophenylazo)N,N-diethylaniline and finally 2.20 parts of sodium cyanide are successively introduced into a reactor. Then the temperature is taken in period of about 45 minutes to 90°C; during the heating, the evolution of the reaction is controlled by thin layer chromatography and it is found that the substitution of the bromine by the

cyanide begins towards 40°C, and that its speed accelerates considerably towards 60°C so that on reaching 90°C, the rate of conversion is 99% with respect to the bromo derivative present at the beginning. The reaction mass is cooled to 20°C, the effect of which is to bring about the crystallisation of the cyano dyestuff. It is filtered off, then washed with 350 parts of water in order to displace the solvent contained in the paste and finally it is dried. 18 parts of 3-acetamido-4-N,N(2'-cyano-4',6'-dinitrophenylazo)-diethylamine are thus obtained. This product titrates 99.6%, its content of the starting halogenated compound is only 0.4% and its content of copper is less than 600 parts per million. The wash water is introduced into a decanter or separator; 120 parts of sodium chloride are added in order that the organic part of the solvent is completely separated, and it is drawn off and united with the fraction of solvent obtained during the filtration. 355 parts of ethyl β-hydroxyethylsulphide are thus recovered, which contains, besides almost all the copper used, about one part of the dissolved cyano azo dyestuff (which takes the overall balance of the reaction to more than 99%).

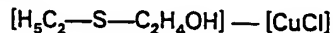
Example 2

The operation is as in Example 1, but starting from the ethyl β-hydroxyethyl sulphide which has just been recovered and of course without adding cuprous chloride. 19 parts of practically pure 3-acetamido-4-N,N(2'-cyano-4',6'-dinitrophenylazo)-diethylaniline are obtained, of which the content of copper is less than 1000 parts per million. The recovery of the ethyl β-hydroxyethyl sulphide and of the copper complex which it contains, under the same conditions as previously described, allows a new reaction. One will thus be able to carry out, for example, more than ten successive operations without appreciable differences being noted in the quality of the solvent and in the reactivity of the catalyst which it contains. The cyano dyestuff is always produced with a yield of over 95%.

Example 3

20 parts of cuprous chloride are stirred into 150 parts of ethyl β-hydroxyethyl sulphide and by light heating to 50°C, a total solution is obtained. After elimination of a few solid particles, the solution is cooled to minus 15°C. A compound slowly separates, which is filtered, washed with a little carbon tetrachloride and then dried at 60°C. 7.5 parts of catalyst are isolated and are present in the form of a greenish powder, the melting point of which is 151.3—153.1°C.

The elementary analysis gave the following composition:



Calculated %;

60 C=23.41 H=4.87 S=15.6 Cu=30.9 Cl=17.3

Found %;

C=23.59 H=4.34 S=15.78 Cu=30.8

Cl=17.19

The principal characteristic absorption bands in the infra-red (KBr) are: 2930 (m), 2890 (m) 2850 (F), 1470 (m), 1458 (m), 1401 (m), 1252 (m), 1075 (F), 1058 (F).

5.77 parts of previously prepared catalyst in the solid state are dissolved in 357 parts of ethyl β-hydroxyethyl sulphide. Next 21.55 parts of 3-acetamido-4-N,N(2'-bromo-4',6'-dinitrophenylazo)-diethylaniline are added and then 2.20 parts of sodium cyanide. The cyanisation is then effected in a manner analogous to that in Example 1. The dyestuff thus prepared is obtained with a yield over 95% and its content of copper is less than 1000 parts per million.

Example 4

80 5.2 parts of cuprous bromide are added to 306 parts of ethyl β-hydroxyethyl sulphide, and the complex is obtained by agitation. Next 20 parts of 3-acetamido-4-N,N(2',6'-dibromo-4'-nitrophenylazo)-diethylaniline are introduced and then 4.2 parts of sodium cyanide. The temperature is taken to 110—115°C and maintained at this for an hour. The total absence of the dibromo derivative initially used can then be controlled by chromatography. 90 After cooling to 20°C, the product formed is separated as in Example 1. 12.3 parts of 3-acetamido-4-N,N(2',6'-dicyano-4'-nitrophenylazo)-diethylaniline are collected of which the content of monocyano derivative is equal to or less than 5%. The recovery of the ethyl β-hydroxyethyl sulphide is 300 parts comprising, besides the copper complex, about 3.5 parts of the dissolved dicyano azo dyestuff (which takes the overall balance of the dicyanisation reaction to more than 95%).

Example 5

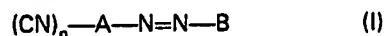
If in Example 1 the ethyl β-hydroxyethyl sulphide is replaced by the same quantity of di-n-propyl sulphide, 13.4 parts of the cyano azo dyestuff are obtained of which the content of copper is less than 1000 parts per million. The di-n-propyl sulphide recovered, as well as the copper which it contains, may be recycled for a further cyanisation reaction.

Example 6

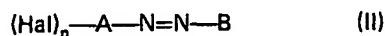
300 parts of methyl hydroxypropyl sulphide, 2 parts of sodium cyanide and 2.39 parts of cuprous chloride are stirred for three hours. Next 15.5 parts of 3-acetamido-4-N,N(2'-bromo-4',6'-dinitrophenylazo)-dihydroxyethylaniline are added and then the mixture is heated at 95°C for an hour. The reaction mass is cooled to 20°C. The cyano dyestuff is filtered off, then washed with water and finally dried. 13 parts of 3-acetamido-4-N,N(2'-cyano-4',6'-dinitrophenylazo)-dihydroxyethylaniline are thus obtained. This product titrates 98% and its content of copper is less than 1000 parts per million. The solvent and the copper are recovered and recycled.

Claims

1. A process for the manufacture of a water-insoluble cyano azo dyestuff of the formula (I)

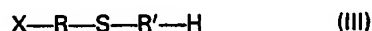


5 which comprises reacting a halogenated azo compound of the formula (II)



10 in which A represents a benzenic radical containing one or more nitrile or halogen substituents in the ortho position with respect to the azo group, Hal represents a halogen atom, B represents the radical of a coupling component, A and B are free from water-solubilising groups and optionally contain other substituents usual in azo dyestuffs and n is 1 or 2 with an alkaline cyanide

15 in a solvent comprising a thioether of the formula (III)



20 where R and R', which may be the same or different, each represent an alkylene radical having from 1 to 8 carbon atoms with a straight or branched chain able to contain a —O— or —S— bridge and X represents a hydrogen atom or a hydroxyl group and in the presence of a catalyst

25 formed by a combination between a thioether of formula (III) and a cuprous salt.

2. A process as claimed in claim 1 in which Hal is bromine, chlorine or iodine.

3. A process as claimed in claim 1 or 2 in which B is a substituted para-amine arylene radical.

30

4. A process as claimed in claim 1, 2 or 3 in which the alkaline cyanide is sodium cyanide.

5. A process as claimed in any of claims 1 to 4, in which the solvent (III) is ethyl β-hydroxyethyl sulphide.

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6. A process as claimed in any of claims 1 to 5 in which the thioether (III) used as a constituent of the catalyst is ethyl β-hydroxyethyl sulphide.

7. A process as claimed in any of claims 1 to 6 in which the temperature of the reaction is from 60°C to 150°C.

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8. A process as claimed in claim 7 in which the temperature of the reaction is from 80% to 100%.

9. A process as claimed in of claims 1 to 8 in which the cuprous salt is cuprous bromide or cuprous chloride.

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10. A process as claimed in any of claims 1 to 9 in which the catalyst is used at the rate of 0.1 to 0.8 atoms of copper contained in the catalyst per mole of halogenated compound (II).

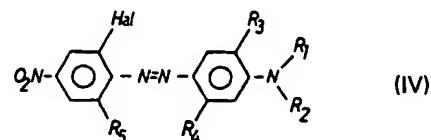
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11. A process as claimed in claim 10 in which the catalyst is used at the rate of 0.25 to 0.5 atoms of copper contained in the catalyst per mole of halogenated compound (II).

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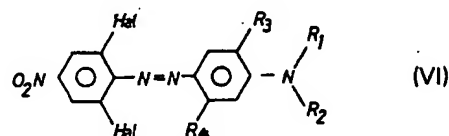
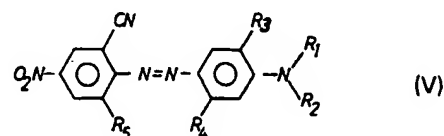
12. A process as claimed in any of claims 1 to 11 in which the catalyst is contained in the solvent used, recycled from the previous operation after separations of the dyestuff (I).

13. A process as claimed in any of claims 1 to 12 in which the cyano azo dyestuff of formula (I) corresponds to the formula (IV):



and the halogenated azo compound of formula (II) corresponds to one of the formulae (V) or (VI).

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where R₁ represents hydrogen, a phenylalkyl group, an unsubstituted alkyl group or an alkyl group substituted by OH, Cl, F, CN, COOR₆, OCOR₆, OCO₂R₆, OR₆ or OCOCH=CH-phenyl, R₂ either has the same significance as R₁ or represents a phenyl or cyclohexyl group; R₃ denotes hydrogen or an alkyl, alkoxy, alkoxy carbonyl, aryloxy or aralkoxy group; R₄ denotes hydrogen, CH₃, OCH₃, OC₂H₅, Cl, NHSO₂R₆, NHCOOR₆ or NHCOR₆; R₅ denotes hydrogen CF₃, COR₆, CN, NO₂ or SO₂R₆ and R₆ is an alkyl, cyclohexyl, phenyl, tolyl, or methoxyphenyl radical.

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14. A process as claimed in claim 13 in which the alkyl group R₁ has 1 to 4 carbon atoms.

15. A process as claimed in claim 13 in which the phenylalkyl group R₁ is one having 1 or 2 carbon atoms in the alkyl group.

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16. A process as claimed in claim 13, 14 or 15 in which R₃ is an alkyl or alkoxy group having 1 to 4 carbon atoms.

17. A process as claimed in claim 13, 14 or 15 in which R₃ is a phenyloxy, phenylmethoxy or phenylethoxy group.

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18. A process as claimed in any of claims 13 to 17 in which the alkyl group R₆ has 1 or 2 carbon atoms.

19. A process for the manufacture of a water-insoluble cyanazo dyestuff substantially as herein described with reference to and as illustrated in any of the Examples.

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20. Dyestuff prepared by a process as claimed in any of claims 1 to 19.

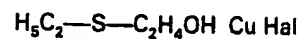
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21. Cellulose ester or polyester coloured with a dyestuff as claimed in claim 20.

22. Copper complexes resulting from the

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combination of a cuprous salt with a thioether of formula (III) as defined in claim 1.



23. Copper complexes of the formula:— 5' in which Hal represents a halogen atom.

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